The Formation Constant of Chromium(III)-Ethylenediamine Complexes

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Many reports have been published on the formation constants of complexes since Bjerrem's theory[1] was presented. Most of them, however, have the concerned complexes formed by divalent metal cations. The formation constants of complexes containing ethylenediamine already reported concern the divalent metals, such as cadmium(II),[2] cobalt(II),[1] iron(II),[1] magnese(II),[1] nickel(II),[2] copper(II),[3] zinc(II)[4] and mercury(II).[5]

As for the formation constants of complexes of the tervalent metals, only the data concerning cobalt(III)[1] and the rare earths are known. As for chromium(III), there has been no formation constant data about either the ethylenediamine complex or complexes with any other ligand.

The divalent metals, in general, form labile complexes, and the velocity of the formation or aquation of the complexes is so large that the conventional pH titration method can be employed to find the formation constants, whereas the tervalent metals such as chromium(III) show a tendency to form substitution-inert complexes because of the smallness of the radius and because the reaction velocity is too small for the pH titration method to be employed. Therefore, the determination of the formation constant of chromium(III)-ethylenediamine complexes has been carried out by means of the photometric method.

Theoretical

Tris(ethylenediamine)chromium(III) perchlorate is thought to be aquated in the aqueous solution according to the three steps expressed by the following equations:

$$[\mathrm{Cr\,en_3}]^{3+} + 2\mathrm{H_2O} \rightleftarrows [\mathrm{Cr(H_2O)_2en_2}]^{3+} + \mathrm{en} \tag{1}$$

$$[\mathrm{Cr(H_2O)_2en_2}]^{3+} + 2\mathrm{H_2O} \rightleftarrows [\mathrm{Cr(H_2O)_4en}]^{3+} + \mathrm{en} \tag{2}$$

$$[\mathrm{Cr(H_2O)_4en}]^{3+} + 2\mathrm{H_2O} \rightleftarrows [\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{en} \tag{3}$$

The measurements of the velocity of these

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[1] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase, Copenhagen (1941).

[2] C. R. Bertsch, W. C. Fernelius and B. P. Block, *J. Phys. Chem.*, **62**, 444 (1958).

[3] J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

[4] C. J. Nyman, E. W. Murbach and G. B. Millard, *J. Am. Chem. Soc.*, **77**, 4194 (1955).

[5] C.J . Nyman, D. K. Roe and D. B. Masson, ibid., **77**, 4191 (1955).

reactions have already been made by Schläfer et al.⁶⁾

In these reactions, when the total concentration of the metal ions is expressed by C_{Cr} and the concentrations of the complex species, hexaaquochromium(III), tetraaquoethylenediaminechromium(III), diaquobis(ethylenediamine)chromium(III) and tris(ethylenediamine)chromium(III), in the solution at equilibrium, by $[\mathrm{Cr(H_2O)_6}^{3+}]$, $[\mathrm{Cr(H_2O)_4en}^{3+}]$, $[\mathrm{Cr(H_2O)_2 \cdot en_2}^{3+}]$ and $[\mathrm{Cr\ en_3}^{3+}]$ respectively, the total concentration, C_{Cr}, is given as:

$$C_{\mathrm{Cr}} = [\mathrm{Cr(H_2O)_6}^{3+}] + [\mathrm{Cr(H_2O)_4en}^{3+}] + [\mathrm{Cr(H_2O)_2en_2}^{3+}] + [\mathrm{Cr\ en_3}^{3+}] \qquad (4)$$

If the molar extinction coefficients of the above four complex species are expressed by ε_1, ε_2, ε_3 and ε_4, and the absorbancy of the solution at equilibrium, by ε, the following relation exists:

$$[\mathrm{Cr(H_2O)_6}^{3+}]\,\varepsilon_1 + [\mathrm{Cr(H_2O)_4en}^{3+}]\,\varepsilon_2 + [\mathrm{Cr(H_2O)_2en_2}^{3+}]\,\varepsilon_3 + [\mathrm{Cr\ en_3}^{3+}]\,\varepsilon_4 = C_{\mathrm{Cr}}\varepsilon \qquad (5)$$

The acid hydrolyses of ethylenediamine are presumed to be expressed by;

$$\mathrm{H_2en^{2+}} \rightleftarrows \mathrm{H^+} + \mathrm{Hen^+} \qquad (6)$$

$$\mathrm{Hen^+} \rightleftarrows \mathrm{H^+} + \mathrm{en} \qquad (7)$$

If the concentration of $\mathrm{H_2en^{2+}}$, $\mathrm{Hen^+}$ and en are expressed by $[\mathrm{H_2en^{2+}}]$, $[\mathrm{Hen^+}]$ and $[\mathrm{en}]$ respectively, the acid dissociation constants of reactions 6 and 7 are given as:

$$k_1 = [\mathrm{H^+}]\,[\mathrm{Hen^+}]/[\mathrm{H_2en^{2+}}] \qquad (8)$$

$$k_2 = [\mathrm{H^+}]\,[\mathrm{en}]/[\mathrm{Hen^+}] \qquad (9)$$

respectively, where $[\mathrm{H^+}]$ is the hydrogen ion concentration.

The concentration of the total of ligand materials, including those involved in the complex formation, C_{en}, is given as:

$$C_{\mathrm{en}} = [\mathrm{H_2en^{2+}}] + [\mathrm{Hen^+}] + [\mathrm{en}] + [\mathrm{Cr(H_2O)_4 \cdot en}^{3+}] + 2\,[\mathrm{Cr(H_2O)_2en_2}^{3+}] + 3\,[\mathrm{Cren_3}^{3+}] \qquad (10)$$

By eliminating $[\mathrm{H_2en^{2+}}]$ and $[\mathrm{Hen^+}]$ from Eqs. 8, 9 and 10, the following relationship is obtained:

$$[\mathrm{en}] = k_1k_2(C_{\mathrm{en}} - [\mathrm{Cr(H_2O)_4en}^{3+}] - 2\,[\mathrm{Cr \cdot (H_2O)_2en_2}^{3+}] - 3\,[\mathrm{Cr\ en_3}^{3+}])/(k_1k_2 + k_1[\mathrm{H^+}] + [\mathrm{H^+}]^2) \qquad (11)$$

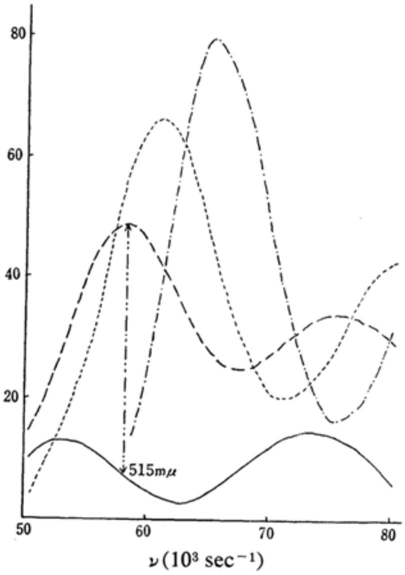

Fig. 1. The absorption spectra of chromium(III)-ethylenediamine complexes.
Hexaaquochromium(III) complex
Tetraaquoethylenediaminechromium(III) complex
Diaquodiethylenediaminechromium(III) complex
Tris-ethylenediaminechromium(III) complex

In order to find the molar extinction coefficients of the tris(ethylenediamine)chromium(III) and aquoethylenediaminechromium(III) complexes, which are formed by the aquation of the former, their absorption spectra must be measured; they are shown in Fig. 1. The absorption spectra of the tris(ethylenediamine)chromium(III) and hexaaquochromium(III) complexes were directly measured, while that of the diaquobis(ethylenediamine)chromium(III) complex was obtained by tracing the aquation of bromoaquobis(ethylenediamine)chromium(III) bromide, which is in good agreement with that reported by Schläfer et al.⁶⁾ The spectra of the tetraaquoethylenediaminechromium(III) complex was obtained by tracing the aquation of the diaquobis(ethylenediamine)chromium(III) complex.

From the absorbancy measured at equilibrium in the prepared solution in order to find the formation constant, the following facts could be inferred: The equilibrium state under the conditions selected by the authors is expressed by Eq. 3; that is to say, the equilibrium mixture consists of the tetraaquoethylenediaminechromium(III) and hexaaquochromium(III) complexes. Even though the solution at equilibrium was contaminated with the diaquobis(ethylenediamine)chromium(III) complex, the impurity is no more than 1% of the two main complexes above, the tetraaquoethylenediamine- and hexaaquochromium(III) complexes.

On the assumption that the equilibrium in solution is accurately expressed by Eq. 3, the

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6) H. L. Schläfer and O. Kling, *Z. phys. Chem.* **16**, 14 (1958).

formation constant was calculated as is shown below.

In this study, it seems reasonable to consider such condition with regard to the concentration of the complex species as:

$$[Cr(H_2O)_2en_2{}^{3+}] \text{ and } [Cr\ en_3{}^{3+}] \ll [Cr(H_2O)_6{}^{3+}] \text{ and } [Cr(H_2O)_4en^{3+}].$$

Taking into account these conditions, Eqs. 4, 5 and 11 are transformed to the following:

$$C_{Cr} = [Cr(H_2O)_6{}^{3+}] + [Cr(H_2O)_4en^{3+}] \quad (12)$$

$$[Cr(H_2O)_6{}^{3+}]\,\varepsilon_1 + [Cr(H_2O)_4en^{3+}]\,\varepsilon_2 = C_{Cr}\varepsilon \quad (13)$$

$$[en] = k_1k_2(C_{en} - C_{Cr})/(k_1k_2 + k_1[H^+] + [H^+]^2) \quad (14)$$

By solving Eqs. 12 and 13 with respect to $[Cr(H_2O)_6{}^{3+}]$ and $[Cr(H_2O)_4en^{3+}]$, the following equations are obtained:

$$[Cr(H_2O)_6{}^{3+}] = C_{Cr}(\varepsilon_2 - \varepsilon)/(\varepsilon_2 - \varepsilon_1) \quad (15)$$

$$[Cr(H_2O)_4en^{3+}] = C_{Cr}(\varepsilon - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1) \quad (16)$$

By substituting for k_1 and k_2 the values given in the literature[4] and by estimating the range of the hydrogen ion concentration measured, the following orders of magnitude are obtained:

$$k_1k_2 \cong 10^{-8},\ k_1[H^+] = 10^{-12} \sim 10^{-10},\ [H^+] \cong 10^{-6} \sim 10^{-4}$$

Therefore, it is reasonable to express the denominator of Eq. 14 by $[H^+]^2$, neglecting the first and second terms.

By substituting Eq. 16 into Eq. 14 after considering the above approximation, the following equation is obtained as the concentration of the free ligand uncomplexing:

$$[en] = k_1k_2\{C_{en} - C_{Cr}(\varepsilon - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1)\}/[H^+]^2 \quad (17)$$

The equilibrium constant of the reaction

$$[Cr(H_2O)_6]^{3+} + en \rightleftarrows [Cr(H_2O)_4en]^{3+} + 2H_2O, \quad (18)$$

which is the reverse of reaction 3, that is to say, the first formation constant, K_1, of the aquoethylenediaminechromium(III) complexes, is given as:

$$K_1 = [Cr(H_2O)_4en^{3+}]/[Cr(H_2O)_6{}^{3+}]\,[en] \quad (19)$$

This formation constant may be calculated by substituting Eqs. 15, 16 and 17 into Eq. 19.

The ionic strengths of the solutions at equilibrium, the absorbancies of which were measured, can be calculated by the following equation;

$$\mu = 1/2\{12\,C_{Cr} + 4\,[H_2en^{2+}] + [HClO_4] + [H^+]\} \quad (20)$$

where $[HClO_4]$ is the concentration of perchloric acid added in order to control the hydroxo-change of the complex. The concentration of ethylenediamine affecting the ionic strength was thought to be only $[H_2en^{2+}]$, for it was found that the concentrations of $[Hen^+]$ and $[en]$ were negligibly small compared with $[H_2en^{2+}]$ when they were estimated by using the first and second acid dissociation constants and the hydrogen ion concentration.

Experimental

Tris(ethylenediamine)chromium(III) Perchlorate.—When chromium(III) chloride hydrate (green) and ethylenediamine were mixed stoichiometrically, the reaction started with a violent evolution of heat. After the mixture had been kept upon an oil bath for three or four hours in order to complete the reaction and the dehydration, a yellowish-brown residue was obtained. When the product was extracted by water, crystalline tris(ethylendiamine)chromium(III) chloride was obtained and purified by recrystallization.

The perchlorate was obtained by adding perchloric acid to the saturated solution of the chloride and by coolin it with ice. It has no water of crystallization. Analytical values: Cr 9.96% (found), 9.80% (calcd.); C 13.87% (found), 13.58% (calcd.); H 4.53% (found), 4.56% (calcd.)

Procedure.—In order to obtain the equilibrium system, a mixed solution of hexaaquochromium(III) salt with ethylenediamine was at first used as the starting material, but the reaction did not proceed. Therefore, the equilibrium state was obtained by aquating the tris(ethylenediamine)-chromium(III) salt prepared above.

The procedure by the latter way as follows. The aqueous solutions of various concentrations of tris(ethylenediamine)chromium(III) perchlorate, to which some quantities of free ethylenediamine had been added to prevent complete aquation and to which an excess amount of perchloric acid had been added to protect the chromium(III) aquo-complexes produced in consequence of the reaction from their hydroxo change, were maintained at 25°C in a thermostat for one or two months. The solutions were always kept in brown flasks to avoid photodecomposition.

The absorbancy of the solution was then measured by means of Hitachi EPS-2 type automatic recording and EPU-2 type spectrophotometers after the equilibrium had been attained. Since it was necessary to find the hydrogen ion concentration of the solution at equilibrium in order to calculate the formation constant, the pH was also measured by means of a Horiba HRL model M pH meter. All the measurements were carried out at 25°C.

Results

The measurement of the absorbancy, ε, of the solution at equilibrium was carried out

Table I. The results of measurements and calculation at 25°C

$C_{Cr}\times10^3$ mol./l.	$C_{en}\times10^3$ mol./l.	ε	$[Cr(H_2O)_4en^{3+}]/[Cr(H_2O)_6{}^{3+}]$	pH	$\log K_1$	$\sqrt{\mu}$
1.986	6.892	32.97	1.726	2.01	16.18	0.2336
2.019	8.393	31.69	1.520	2.05	15.94	0.2395
2.436	8.242	33.86	1.897	2.09	15.99	0.2415
2.019	10.73	31.20	1.449	2.31	16.27	0.2442
3.830	13.83	36.16	2.423	1.85	16.37	0.2817
3.770	12.24	35.28	2.199	1.67	16.74	0.2835
3.790	16.04	36.15	2.425	1.82	16.35	0.2901
5.081	19.91	34.76	2.064	1.80	16.23	0.3126
4.785	18.91	41.59	5.074	1.72	16.81	0.3537
4.293	12.88	31.09	1.434	1.20	17.48	0.3689
4.206	21.96	36.98	2.667	1.29	17.28	0.3805
4.236	31.39	33.64	1.848	1.42	16.71	0.3963

at the wave length of 515 mμ, where the difference in absorbancy between hexaaquochromium(III) and tetraaquoethylenediaminechromium(III) complex is the greatest, as may be seen in Fig. 1. As the molar extinction coefficients of these two complexes in the solution at this wave length, $\log \varepsilon_1=5.97$ and $\log \varepsilon_2=48.59$ were used respectively.

As the acid dissociation constants of the first and second steps of ethylenediamine, $pk_1=7.42$ and $pk_2=10.14$[4] were employed respectively.

In order to calculate the value of [en] by inserting into Eq. 17 the measured absorbancy, ε, the acid dissociation constants pk_1 and pk_2 given above, and the total concentrations of chromium(III) salts and ethylenediamine, it is necessary to known the hydrogen ion concentration, $[H^+]$. What is obtained by pH measurement is not $[H^+]$, but the activity. Therefore, [en] was first calculated by inserting the value of the activity instead of the value of hydrogen ion concentration into $[H^+]$ in Eq. 17; then the equilibrium constant, K_1, was obtained by applying the value of [en] to Eqs. 15, 16 and 19. The ionic strength was calculated at the same time by means of Eq. 20.

Subsequently, the activity coefficient of the hydrogen ions at each ionic strength calculated as above was obtained from Kielland's table.[7] After the hydrogen ion concentration, $[H^+]$, had been obtained by dividing the activity by its activity coefficient, the equilibrium constant, K_1, was recalculated by inserting the hydrogen ion concentration into Eq. 17 and by computing the value of Eq. 19.

The values obtained by these measurements and those calculated from them are listed in Table I.

The logarithm of the equilibrium constant, K_1, is plotted against the square root of the ionic strength in Fig. 2.

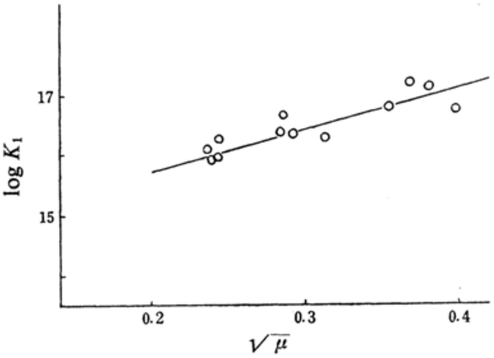

Fig. 2. The relationship between the logarithm of the equilibrium constant and the square root of ionic strength.

The formation constant of the second step of aquoethylenediaminechromium(III) complexes could not be determined spectrophotometrically. The exact formation constants could not be obtained by pH measurements alone, because the error in calculation was too large at low pH values, while decomposition easily occurred at high pH values; consequently, the pH range which gave exact values of formation constants was too restricted. As the rough value of the formation constant of the second step at the ionic strength of $\mu=0.1$, $\log K_2<14$ was obtained.

Discussion

It may be seen in Fig. 2 that the formation constants of the first step of aquo-ethylenediaminechromium(III) complexes at the ionic strength of $\mu=0.05$, 0.10 and 0.15 are given by $\log K_1=15.9$, 16.5 and 17.0 respectively. As may be seen from these values, the equilibrium constant, K_1, does not depend much on the ionic strength of the solution.

This may be explained by the fact that the hexaaquochromium(III) and tetraaquoethylenediamine chromium(III) complexes, which give

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[7] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

TABLE II. FORMATION CONSTANTS OF ETHYLENDIAMINE COMPLEXES OF TERVALENT CHROMIUM OR COBALT AND DIVALENT CHROMIUM AND COBALT

	log K_1	log K_2	log K_3	Condition	
Cr(III)	16.5	<14	—	$\mu=0.1$,	25°C
Co(III)	18.7	16.2	13.8	$\mu=1.0$,	30°C[9]
Cr(II)	5.145	4.035	—	$\mu=1.4$,	25°C[10]
Co(II)	5.93	4.73	3.30	$\mu=1.0$,	25°C[11]

the respective concentrations, $[Cr(H_2O)_6^{3+}]$ and $[Cr(H_2O)_4en^{3+}]$, in the numerator and denominator of Eq. 19 respectively, are both tervalent cations and by the assumption that the ionic radii of these complex cations are approximately equal.

The formation constants of the aquo-ethylenediaminechromium(III) complexes obtained are listed in Table II, together with those of the corresponding cobalt(III) complexes and the ethylenediamine complexes of divalent chromium and cobalt.

Table II shows, in the first place, that the formation constants of the aquo-ethylenediamine complexes of tervalent chromium and cobalt are far larger than those of the corresponding divalent metal complexes. This must be due to the fact that the covalency of the coordinated bond of the ligand with tervalent metal ions is much stronger than that with divalent ions because of the smaller radii of the former ions.

The Table also shows that the formation constants of the aquo-ethylenediaminechromium(III) complexes are a little smaller than those of the corresponding cobalt(III) complexes. On the other hand, it has already been found[8] that the crystal-field stabilization energy of the tris(ethylenediamine)chromium(III) complex is much smaller than that of the tris(ethylenediamine)cobalt(III) complex. This means that the formation constants of these two complexes can not be determined only by means of the crystal field stabilization energy. In addition, in order to explain the difference in stability between these chromium(III) and cobalt(III) complexes, the following concept is effective: The cobalt complexes are instabilized by the mutual repulsion of the six 3d electrons paired in the bonding orbitals more than the corresponding chromium(III) complexes which have unpaired three electrons; that is to say, the contribution of Racah's electrostatic parameter upon the crystal-field stabilization is greater in the cobalt(III) complex than in the chromium(III) complex.

Summary

1) The formation constants of chromium (III) complexes with ethylenediamine, the simplest bidentate ligand material coordinated by two nitrogen atoms, have been spectrophotometrically determined.

2) It has been shown that the dependence of the formation constant of the first step upon the ionic strength is small.

3) The formation constants of the chromium(III) complexes with ethylenediamine have been found to be remarkably higher than those of the corresponding chromium(II) complexes and a little lower than those of the corresponding cobalt(III) complexes.

4) The difference between the formation constants of the chromium(III) and cobalt(III) ethylenediamine complexes has been qualitatively explained with reference to the crystal-field stabilization energy and to Racah's electrostatic repulsive parameter.

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[8] C. K. Jørgensen, "Energy Levels of Complexes and Gaseous Ions," Jul. Gjellerups Forlag, Copenhagen (1957).

[9] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand*,. 6, 1265 (1952).

[10] R. L. Pecsok and J. Bjerrum, ibid., 11, 1419 (1957).

[11] L. J. Edwards, Diss., Univ. Michigan, 1950.